Disturbing the dimers: electron- and hole-doping in the nonmagnetic intermetallic insulator $FeGa_3$

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The nonmagnetic "intermetallic insulator" $FeGa_3$ poses several peculiar puzzles. The insulating phase can be described at the most basic level by either the uncorrelated limit or the strongly correlated limit of density functional theory viewpoints, where the latter corresponds to a non-magnetic singlet on the Fe_2 dimers. No reasonable *charge state* picture of Fe works at this stoichiometry, which we reconcile with a Wannier function (WF) analysis that puts a single dimer-centered WF on each dimer, corresponding to a half-integer charge state if taken literally. Our density functional based calculations reveal rich behavior of the system upon electron and hole doping, whether by Ge and Zn on the Ga site or by Co and Mn doping on the Fe site. The obtained behavior depends strongly on whether strong on-site repulsion effects are included.Magnetism appears readily with doping, with half metallic phases providing part of unexpected behavior.

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I. BACKGROUND

$FeGa_3$ is a rare non-magnetic intermetallic insulator that has attracted particular attention due to its unusual transport and magnetic behavior. This Fe-based material exhibits non-conducting behavior with reported narrow gap in the 0.3-0.55 eV range.[?] [?] Particular attention has been paid to understand the mechanism of the gap formation that has been discussed in the context of strong hybridization between Fe-3d and Ga-4p orbitals, reminiscent of that in strongly correlated 3d and 4f Kondo insulators,[?] and it has been suggested there are magnetic correlations present in spite of the observed diamagnetic ground state.

Given the small band gap and the presence of very narrow bands around the Fermi level, $FeGa_3$ has been most extensively studied as a thermoelectric material. High values of the Seebeck coefficient around 350 μV/K have been predicted at room temperature.[?] Its narrow gap and unusual properties suggesting electronic correlations brings to mind related iron compounds FeSi[?] [?] [?] and $FeSb_2$,[?] [?] whose underlying electronic systems remain to be understood.

There is no unambiguous picture of the electronic and magnetic (or not) character of stoichiometric $FeGa_3$. According to susceptibility measurements, $FeGa_3$ is diamagnetic below room temperature (RT) and the susceptibility shows an increase above RT suggesting the proximity to a crossover to a paramagnetic metallic state.[?] Fe Mössbauer spectra did not show the presence of an internal magnetic field at the Fe site, supporting a nonmagnetic state of Fe[?] though not ruling out exotic correlated states. In contrast, muon spin rotation studies detected spectroscopic features interpreted in terms of electron confinement into spin polarons that requires the existence of Fe moments.[?]

Hole or electron doping drastically changes the properties of the parent compound, giving rise to emergent magnetic phases. Replacing Fe breaks the dimer symmetry, a fundamental impact *if* there is important Fe-Fe bonding or singlet formation. Focusing first on electron doping, Co-substitution for Fe induces an insulator-to-metal transition.[?] [?] [?] Resistivity $\rho(T)$ measurements for $Fe_{1-x}Co_xGa_3$ are not yet conclusive; reports indicate the metallic state is reached at doping level x=0.025-0.075[?] or possibly even at a higher doping level x=0.125[?] or 0.23.[?]

Analysis of the T-dependence of the nuclear spin-lattice relaxation rate $1/T_1$ of the ^{69,71}Ga nuclei suggest the existence at low doping of in-gap states.[?] In $Fe_{0.5}Co_{0.5}Ga_3$, the relaxation is strongly enhanced due to spin fluctuations, often a signature of a weakly antiferromagnetic metal. Such itinerant antiferromagnetic behavior contrasts with both magnetization measurements, showing localized magnetism with a relatively low effective moment of 0.7 μ_B/f.u, and DFT calculations that predict a ferromagnetic state with an ordered moment of 0.5 μ_B/f.u. The simplest picture is that Co doping shifts the Fermi level position towards the conduction band formed by Fe and Co-3d with Ga-4p admixture that is essential for gap formation.

Electron-doping by substituting Ga by Ge leads to drastically different behavior.[?] [?] Conductivity is found at an extremely low doping level y= 0.0006, progressing to a weak ferromagnetic order at y_c= 0.13 which never appears in the Co-doped compound for 0≤x≤1. The emergence of the FM state is accompanied by quantum critical behavior observed in the specific heat and the magnetic susceptibility. The FM instability found in in $FeGa_{3-y}Ge_y$ beyond

y_c= 0.13 indicates that strong electron correlations are induced by the disturbance of Fe $3d$ – Ga $4p$ hybridization, or possibly that existing strong correlations are disrupted.[?]

Turning now to non-stoichiometry, Gamza *et al.*[?] performed resistivity and thermodynamic measurements on single crystals of $FeGa_3$, $Fe_{1-x}Mn_xGa_3$ and $FeGa_{3-y}Zn_y$ (x $\leq$ 0.12 and y $\leq$ 0.06). Unlike for electron doping, hole doping using Mn on the Fe site or Zn on the Ga site does not induce a semiconductor-to-metal transition. Hole doping induces states into the semiconducting gap that remain localized at the highest doping levels. Using neutron powder diffraction measurements, they conclude that $FeGa_3$ orders magnetically above room temperature in a complex structure, unaffected by the inclusion of Mn and Zn. According to dynamical mean field theory (DMFT) calculations[?] Fe ions in $FeGa_3$ are dominantly in an S=1 state but being subjected to strong spin and charge fluctuations. Itinerant magnetism for the spin response is proposed due to the small contributions of local spin fluctuations to the spin susceptibility.

Evidently input from theoretical modeling is required to move toward understanding of this unusual behavior. Density functional theory (DFT) based calculations performed within LDA in undoped $FeGa_3$ reproduce the value of the band gap (0.4-0.5 eV) with no magnetism involved.[?] Within the correlated DFT LDA+U method (see Sec. III), local Fe moments arise on Fe if they are allowed to be antialigned ("antiferromagnetic" [AFM]). At low values of U, the moments are somewhat below 1 μ_B, consistent with spin S=1/2). In view of these results, Yin and Pickett[?] suggested that the Fe dimers could be forming spin singlets with S_{tot}=0 and that magnetism found in doped $FeGa_3$ would be linked to the breaking of the singlets leading to free spins. Singh showed[?] that the magnetism of some types of doping of $FeGa_3$ can be explained within GGA without the need of spin coupling of pre-existing moments. This weakly correlated picture suggests that both n-type and p-type $FeGa_3$ will become itinerant ferromagnets[?] due to the large density of states on either side of the gap.

As a brief review, we note that DFT-based calculations have been performed in $FeGa_3$ using the two more common (semi)local approaches for the exchange correlation energy and potential: local density approximation (LDA) or generalized gradient approximation (GGA).[?, ?] Either seems to be sufficient for describing the electronic structure of the undoped compound. However, they are not able to model the AFM phase in Co-doped $FeGa_3$, and they incorrectly predict a metallic FM ground state for hole doped $FeGa_3$, whether by Ga or Fe substitution. The use of a non-multiplicative (non-local) potential such as LDA+U and the explanation in terms of an antiferromagnetic ground state for undoped $FeGa_3$[?] based on LDA+U calculations introduces new question. Singh obtained magnetic states in doped $FeGa_3$ using GGA alone. In this paper we revisit several aspects of the electronic structure of electron and hole-doped $FeGa_3$, comparing results from the LDA and LDA+U functional forms. Because in several cases the value of the gap is of some importance, in the appendix we indicate how the modified Becke Johnson potential (see within) shifts bands and in some cases modifies magnetic moments.

II. STRUCTURE

$FeGa_3$ crystallizes in the tetragonal space group $P4_2/mnm$. Its lattice constants are a= 6.2628 Å and c= 6.5546 Å with four formula units (two Fe_2 dimers) per unit cell. Fe atoms are at (0.3437, 0.3437, 0) and form dimer pairs in the z=0 plane along (110) and in z= 1/2 along the (1$\bar{1}$0) directions, as illustrated in Fig. 2. There are two inequivalent Ga sites: higher symmetry Ga1 at (0, 0.5, 0), and lower symmetry Ga2 at (0.1556, 0.1556, 0.262). Each Fe atom has eight Ga neighbors, at distances of 2.36(2), 2.39(2) and 2.50(4) Å. The paired Fe atoms are separated by 2.77 Å, 12 % larger distance than that between Fe atoms in bcc Fe metal (2.48 Å).

FIG. 1: (Color online) Crystal structure of the unit cell of $FeGa_3$, viewed approximately down the c-axis. Fe atoms form dimers oriented along the [110] and [1$\bar{1}$0] directions. The local coordinate system used in the DOS plots with the local z axis directed along the Fe-Fe dimers is shown near the center of the figure. There are two distinct sites for Ga atoms.

III. COMPUTATIONAL METHODS

The electronic structure calculations were performed with the WIEN2k code,[?] [?] based on density functional theory (DFT) utilizing the augmented plane wave plus local orbitals method (APW+lo).[?] The calculations were well converged with respect to the k-mesh and $R_{mt}K_{max}$=7.0 cutoff. Selected sphere radii (a.u.) were the following: 2.27 for Fe, 2.16 for Ga, 2.35 for Mn and Co, 2.16 for Ge, and 2.22 for Zn.

Because the description of the electronic structure is in question, an assortment of exchange-correlation potentials have been used: LDA,[?] LDA+U (LDA plus the on-site repulsion U),[?] and TB-mBJ included with LDA. The LDA+U scheme improves over GGA or LDA in the study of systems containing strong intraatomic repulsion such as occur in many transition metal compounds.[?] [?] We have performed calculations on $FeGa_3$ electron and hole doped within the LDA+U method taking U in a reasonable range for this type of 3d electron system (3-6 eV). The Hund's rule J was fixed at 0.7 eV. The modified Becke-Johnson exchange potential (a local approximation to an atomic exact-exchange potential and a screening term) + LDA correlation (from hereon TB-mBJ) allows the calculation of band gaps with an accuracy similar to the much more expensive GW or hybrid methods.[?] [?] We have also studied the electronic structure of doped $FeGa_3$ by using the TB-mBJ potential which does not contain any system-dependent parameter.

IV. STOICHIOMETRIC FEGA$_3$

Both ferromagnetic and antiferromagnetic orientations within the Fe_2 dimers have been studied. Within LDA (GGA) only a nonmagnetic solution can be stabilized. This result is consistent with the observed diamagnetism in pure $FeGa_3$ and with previous electronic structure calculations.[?] [?] In Fig. 2 the band structure with band character plot and DOS of $FeGa_3$ within LDA are shown. The electronic state is insulating with a band gap of 0.45 eV.

Flat bands both below and above the gap give rise to a large DOS into which electrons or holes will be doped. Most of the contribution to states around the Fermi level comes from narrow Fe-d bands with little Ga-p contribution. A very wide Ga 4p band (not shown) can be seen in the valence band region with a width of 10 eV. For Fe 3d states we use a local coordinate system with the local z axis oriented along the dimer axis. Using this local coordinate system the DOS looks as shown in the bottom panel of Fig.2 with seemingly pseudo-cubic d_{xy}, d_{xz}, d_{yz} occupation. Below the gap, occupied d_{xz}, d_{yz} bands form a narrow, 0.35 eV wide four-band/spin complex. Above the gap, d_{z^2} and $d_{x^2-y^2}$ bands form a 0.4 eV wide two-band/spin complex. This different orbital character has been pointed out earlier by Yin and Pickett and by Singh.[?] [?]

FIG. 2: (Color online) Left panel: band structure with band character plot (Fe highlighted) of non-magnetic $FeGa_3$ within LDA, illustrating the predicted band gap that is in agreement with experiment. Right panel: Orbital resolved DOS for Fe orbitals, in local coordinates for nonmagnetic $FeGa_3$ and obtained within LDA.

A. Analysis of band character

In halides, oxides, and some chalcogenides of iron, it is possible and very useful to identify the charge state (also known as formal valence) of Fe. This underlying picture provides substantial guidelines on the character of excitations that are likely to dominate the low energy behavior of the system. In some unusual (semi)metallic transition metal compound, viz. $CoSb_3$,[?] such identification proves to be difficult, with unconventional pictures arising. We preface our study of doping of $FeGa_3$ with information relating to the Fe charge state (3d occupation). We remind that the formal charge state often has only a very indirect connection to the physical charge density of atoms in the compound.[?]

The integrated partial DOS, obtained from the fatband character of the Bloch states, provides a guideline on the 3d occupation of Fe. Supposing

TABLE I: Band gap (in eV), and Fe/Mn/Co atomic moment (in μ_B) for the magnetic ground state of undoped and hole/electron doped $FeGa_3$ within LDA and mBJ.

	MM Fe1/Fe2	MM Fe3/Fe4	MMTOT	GAP
$FeGa_3$				
LDA	0.00/0.00	0.00/0.00	0	0.45
mBJ	0.00/0.00	0.00/0.00	0	0.57
$FeGa_{2.75}Zn_{0.25}$				
LDA	0.40/0.40	0.00/0.00	0.8	0
mBJ	1.00/1.00	-0.50/-0.50	1.0	0.2
$FeGa_{2.5}Zn_{0.5}$				
LDA	0.75/0.75	0.07/0.34	1.0	0
mBJ	1.28/1.28	0.77/-0.95	2.0	0
$FeGa_{2.5}Ge_{0.5}$				
LDA	0.39/0.39	0.43/0.37	2.0	0
$FeGa_{2.75}Ge_{0.25}$				
LDA	0.22/0.22	0.23/0.23	0.9	0
mBJ	0.42/0.42	0.20/0.20	1.0	0
	MM Mn,Co/Fe2	MM Fe3/Fe4	MMTOT	GAP
$Fe_{0.75}Mn_{0.25}Ga_3$				
LDA	0.76/0.26	0/0	1.0	0
mBJ	1.28/0.38	-0.30/-0.30	1.0	0
$Fe_{0.75}Co_{0.25}Ga_3$				
LDA	0.17/0.34	0.20/0.20	0.9	0
mBJ	0.17/0.50	0.23/0.23	1.0	0

that true $3d$ character falls off above 1.5 eV, with higher lying d character reflecting tails of Ga atoms extending into the Fe sphere, the d_{xy}, d_{xz}, d_{yz} orbitals are fully occupied, 6 e^-/Fe. The other two orbitals, local d_{z^2} and $d_{x^2-y^2}$ (which are very distinct orientationally and probably chemically), are 75 % occupied, thus providing 1.5 e^-/Fe. The inferred occupation is then a surprising Fe−14d^9. This characterization would be $(Fe_2)^{-2}$ $(Ga_6^{+2}$. This characterization is not outrageous – Ga is quite electropositive and easily donates electrons to neighboring electronegative atoms. This picture can be given further scrutiny.

B. Fe−Fe dimer from Wannier function perspective

There are, incontrovertibly, 17 occupied bands per spin channel per Fe-Fe dimer cluster. This situation, and especially the gap obtained even in the weakly correlated limit, strongly suggests covalent (or metallic) bonding rather than ionic bonding as in many Fe compounds. Since we could only assign orbitals localized at specific sites in the initial projection to obtain WFs, our choice was to have 4 electrons per Fe, two electrons for six of the Gas and one electron for the other six Gas. Often these "basic" associations do not persist, as was the case here. The band structure obtained from Wannier function interpolation agrees with the band structure obtained from DFT calculations (see Fig. 3), indicating a faithful (though not necessarily unique) transformation to WFs. Of the 17 Wannier functions/spin, precisely one is located in the middle of the Fe-Fe dimer, i.e. one per Fe-Fe dimer as can be seen in Fig. 4, or 1/2 electron per Fe. The other 16 Wannier functions/spin resemble each other to certain degree: lopsided with much of the occupation assignable to the Fe site.

This result suggests a *half-integer* formal valence, *i.e.* an Fe_2 charge of $p + \frac{1}{2}$ where p is integer contribution from the other 16 WFs. There is no restriction however that these other 16 WFs must be assignable to an integer occupation of Fe and Ga states. If p=4 (say), then the six Ga atoms contribute 16-2p=8 electrons, *i.e.* 1.33 each, leading to an unsatisfactory picture. Other possible choices of p also lead to unphysical values. A half-integer valence, if it makes sense anywhere, certainly does not account for the insulating behavior.

We conclude therefore that no simple Fe charge state picture works for $FeGa_3$. The strong separation between occupied pseudocubic "t_{2g}" orbitals and empty "e_g" orbitals is a distinguishing feature of the Fe_2 dimer, as is strong mixing with the Ga $s-p$ orbitals.

FIG. 3: Comparison between the band structure obtained from DFT calculation and Wannier function interpolation. Note: The k-mesh used in Wannier function calculation does not necessarily include the k-points in band structure calculation. Therefore, whether the interpolated band structure from Wannier functions calculation agrees with the DFT calculation could be used as a measure of reasonableness of Wannier function calculation

FIG. 4: Left panel: Wannier function representing Fe-Fe bonding orbital (for one Fe_2 dimer) linked to the bonding d_{z^2}-$d_{x^2-y^2}$ occupied below the set of $d_{xz,yz,xy}$ (in local coordinate system). Right panel: example of Wannier function shared between Fe-Ga atoms

FIG. 5: Isosurface plots of states in $FeGa_3$. Left panel: charge density obtained using XCRYSDEN[?] corresponding to the states at the bottom of the gap in $FeGa_3$. Right panel: charge density of the states just above the gap in $FeGa_3$. The strong directionality of the charge along the Fe-Fe bond is evident. While the charge remains localized around Fe atoms, the differing characters of the contributing states is obvious.

C. Charge density of flat near-gap bands

Figure 5 shows 3D isosurfaces of the charge density for the narrow Fe $3d$-dominated bands just below and just above the gap. Consistent with the discussion provided above, the occupied states are a mixture of pseudocubic d_{xz} and d_{yz} charge, with smaller contribution from d_{xy}, and is roughly circular in cross section around the dimer axis. The unoccupied states are a combination of “pseudocubic e_g” states: d_{z^2} orbitals directed along the dimer axis, and $d_{x^2-y^2}$ with lobes perpendicular to the dimer axis. This density is decidedly non-circular in cross section. Both densities reflect antibonding character, or at least nonbonding character, with no evidence of bonding charge. There is negligible contribution to the density that is displayed from Ga sites. The very small dispersion of the bands bordering the gap suggest molecular orbitals as the basic underlying feature for near-gap states.

V. DOPING TREATED WITHIN LDA

We have performed supercell calculations in which both $4p$ (Ga) and $3d$ (Fe) substitutional doping mechanisms have been explored: either Ge or Zn were substituted on Ga1 or Ga2 sites (y= 0.25, 0.5) and Fe was substituted by either one (two) Co or one (two) Mn (x= 0.25, 0.5).

Within LDA our results are consistent with those presented by Singh within GGA.[?] Due to the steep and large DOS on either side of the gap, a FM half metallic (HM) solution is obtained in all cases of low doping (Stoner mechanism for itinerant ferromagnetism). The magnetic solution is different for the two types of directions of doping, as we will describe below.

A. Hole doping Fe→Mn

When one of the three Fe atoms in the unit cell being replaced by Mn, only a FM ordered state within the Mn-Fe pair can be stabilized using LDA. A moment (we quote values within the respective atomic

FIG. 6: Orbital resolved DOS for Mn atoms in local coordinates for $Fe_{0.75}Mn_{0.25}Ga_3$ within LDA (top panel) and LDA+U (U= 3 eV). Hole doping shifts the Fermi level into the four-band complex with d_{xy}, d_{xz}, d_{yz} character for the minority spin channel giving rise to a half metallic solution. The onsite Coulomb repulsion causes shifts in the band structure of 1 eV and introduces e_g-like states in the gap for the minority spin channel

spheres) of $0.76\mu_B$ is obtained. (see Table I) The Fe paired with the Mn has an induced moment of 0.26 μ_B, whereas the other Fe_2 dimer remains nonmagnetic.

This doping gives rise to both Mn and Fe states crossing the Fermi level. Fig. 6 shows the DOS for Mn exhibiting a simple exchange-splitting plus rigid-band behavior characteristic of an itinerant FM within LDA (GGA). The single hole difference leaves E_F lying with the four $3d$ bands of the metallic minority spin channel, which are very strongly Mn character – the hole remains on the Mn atom. The exchange splitting is about 0.25 eV. The majority spin channel remains insulating with a gap of 0.5 eV.

This HM solution agrees with the suggestion of previous DFT-based calculations from VCA,[?] but disagrees with experiments that show that upon Mn doping, a semiconducting state of $FeGa_3$ is retained – no insulator-metal transitions occurs.

B. Electron doping Fe→Co

Low level electron doping with Co for Fe gives a simple rigid band shift downward of the majority spin channel. The extra electron of Co goes into the majority valence band, which is exchange split by 0.2 eV and is nearly HM. The state is ferromagnetic, with moments on the Co/Fe pair of $0.17/0.34\mu_B$ and $0.20\mu_B$ for each Fe on the Fe_2 dimer. In this case the electron is less localized than the hole on Mn, and the total moment of nearly 1 μ is spread rather weakly across all transition metal ions.

FIG. 7: Orbital resolved DOS for Co atoms in local coordinates in $Fe_{0.75}Co_{0.25}Ga_3$ within LDA (upper panel) and LDA+U (lower panel). Electron doping simply drives the Fermi level into the conduction band, thereby resulting in insulator-metal transition.

C. Hole doping: Ga→Zn

Ga1 substitution by Zn corresponds to a doping level x= 0.25, and Zn has a pair of Fe atoms at a distance of 2.36Å. Ga2 substitution corresponds to a doping level x= 0.5, and has also a pair of Fe at a short distance of 2.50 Å and one of the Fe of the other pair at 2.39 Å. Experimental data on Mn- and Zn-doped $FeGa_3$ differ from the LDA-based predictions of emergence of a HM FM state. p-type doping shifts the Fermi level into the valence band and metallic behavior, whereas transport measurements for $FeGa_{3-y}Zn_y$ ($y \leq 0.06$) and $Fe_{1-x}Mn_xGa_3$ ($x \leq 0.12$) show no insulator-metal transition, but instead semiconducting behavior with electrical resistivities determined by the presence of localized in-gap states even for the highest doping levels reached in experiments.

When hole doping on the Ga site, only a half metallic FM solution can again be stabilized. For y=0.25 moments of $0.40\mu_B$ are induced in the pair of Fe atoms closer to Zn whereas the other Fe-Fe pair becomes *nonmagnetic*. For $y = 0.50$, moments of $0.75\mu_B$ are obtained in the Fe pair at 2.50Åand a moment of $0.34\mu_B$ in the Fe at 2.40Å. The Fe far from the Zn atom (at 4.58 Å) remains nonmagnetic. Magnetism arises again from the t_{2g} orbitals, with larger contribution from the d_{yz} orbital at the Fermi level for every magnetic Fe.

For the lower doping level, the half metallic FM state appearing for Ga ($4p$) substitution is very similar to that corresponding to Fe ($3d$) substitution (x, y= 0.25). The rigid band behavior obtained upon hole doping is however lost when the doping level increases to y=0.5 with a widening of the valence band right below the Fermi level in the majority spin channel.

D. Electron doping: Ga→Ge

FIG. 8: Orbital resolved DOS for the non-equivalent Fe atoms in local coordinates for $FeGa_{2.5}Ge_{0.5}$ obtained within LDA. The upper two panels are the PDOS of Fe1 and Fe2 with the partially occupied d_{z^2} and $d_{x^2-y^2}$. The bottom panel is PDOS of Fe3/Fe4. Electron doping through Ge substitution pushes the Fermi level into the conduction band for both spin channels and induces magnetic moments on Fe due to exchange splitting.

From experiments, Co-doped $FeGa_3$ is different from the Ge-doped counterpart. The Ge-doped compounds are ferromagnetic with a positive Curie Weiss temperature as noted in the Introduction. To study the effects of electron doping on the Ga site, we carried out supercell calculations with Ge substitution at Ga1 (y=0.25) and Ga2 (y=0.5). Calculations within LDA lead to ferromagnetic alignment of moments that are equally distributed among all Fe atoms, unlike the case of hole doping where Fe atoms closer to the substituted Zn atom were prone to yield a higher magnetic moment. For $y = 0.25$ Fe atoms exhibit magnetic moments of 0.2 μ_B, for $y = 0.5$ moments of 0.4 are developed.

The same type of half metallic solutions described for the Co-doped compound are obtained with noticeably different splittings for d_{z^2}-$_{x^2-y^2}$ orbitals due to the change in local environment as can be seen in Fig. 8.

VI. DOPING ON THE FE SITE: EFFECT OF CORRELATIONS

The scenario in which semiconducting $FeGa_3$ is antiferromagnetic with the Fe dimers forming singlets was proposed by Yin and Pickett based on LDA+U calculations.[?] For the stoichiometric compound LDA and LDA+U give very similar band gaps consistent with experiment, with the DOSs differing only in some specifics. Thus possible effects of strong on-site repulsion and the resulting correlation effects remain an open question. When doping occurs, and especially when substitution is done on the Fe site, effects of correlation are likely to become more evident. We pursue this question in this section.

We have calculated the effective U for $FeGa_2$ using the approach proposed by Madsen and Novak[?] for augmented plane wave methods based on the procedure suggested by Anisimov and Gunnarsson.[?] In this method the occupation of a target orbital (in this case the $3d$ orbitals of Fe) is enforced. Due to the ambiguity in the charge state of Fe described above, different $3d$ occupations from d^8 to d^5 were presumed, with resulting effective U values increasing linearly from 2 to 5 eV, respectively. We have performed calculations using the fully localized limit double counting functional within this U range, with J being set to 0.8 eV for Fe. We will focus first on the results obtained for U=2 eV, J=0.8 eV since that is what was calculated for $3d$ occupation d^8 that seems in better agreement with the description of the electronic structure. A derived U value from photoemission experiments is 3 eV.[?]

For the undoped compound, when an onsite Coulomb repulsion is included, a magnetic solution can only be obtained for antialigned moments within the dimers. The magnetic moments vanish when FM order is set, for the values of U studied here. The magnitude of the magnetic moment increases gradually as the U value does (from $0.5\mu_B$ for $U = 2$ eV, to $1.07\mu_B$ for $U =$ 3eV, and $1.63\mu_B$ for $U =$ 4 eV). The derived magnetic moments are in agreement with those obtained by Yin *et al.*[?] An insulating state is retained for U in the 2-4 eV range, but surprisingly the band gap closes as U increases. The changes in electronic structure can be roughly considered as rigid-like shifts in the bands.

For electron (Co) or hole (Mn) doping on the Fe site, for the lower U value of 2 eV, only FM ordering within the pairs is obtained. A strong moment of $1.43\mu_B$ on Mn (S=$\frac{3}{2}$) contrasts with a low spin (S=0) moment of $0.15\mu_B$ on Co. The moments on the neighboring Fe ion remain low spin $\sim 0.2\mu_B$ in both cases. The resulting electronic structure has the same features as that obtained within LDA: a HM FM state. Thus at U=2 eV correlation effects do not appear to be significant. For $U \geq 3$ eV the picture changes qualitatively. Not only can both FM and AFM alignments within the dimers be obtained, but the AFM alignment becomes energetically favored.

Mn substitution. Now we consider U=3 eV unless otherwise stated. The lower panel of Fig. 6 shows the LDA+U orbital resolved density of states in the local coordinate system for AFM alignment in $\mathrm{Fe_{0.75}Mn_{0.25}Ga_3}$. While HM character remains, the onsite Coulomb repulsion shifts certain d bands by more than 1 eV giving rise to distinctive changes in configuration. A band with $d_{x^2-y^2}$ character appears within the gap in the minority spin channel, in contrast to the LDA case, whose DOS is shown in the upper panel of Fig. 6. The complete $d_{x^2-y^2}$ spectral density within the gap strongly implies that for an isolated Mn dopant (*i.e.* the low doping limit) an unoccupied $d_{x^2-y^2}$ gap state will appear, perhaps near mid-gap.

Contrasting the LDA+U magnetic character to that of LDA, the magnetic moment of Mn (Fe) increases from 1.43 to $2.10\mu_B$ (respectively, from 0.2 to $0.9\mu_B$). For FM alignment at the same U= 3 eV value (which is energetically higher by 30 meV/Mn) the Fe moments are reduced to $\sim 0.5\mu_B$ reflecting substantial itinerant character of the magnetism. The band shifts are even more noticeable for higher U values, with the majority gap closing accompanied by an increase in the magnetic moments of Mn and Fe that reach values of $3.00\mu_B$ and $2.05\mu_B$, respectively.

Co substitution. The lower panel of Fig. 7 shows the orbital resolved DOS for the LDA+U AFM ground state for $\mathrm{Fe_{0.75}Co_{0.25}Ga_3}$. The picture upon electron doping appears somewhat simpler than for hole doping: the various orbital projected densities of states can be visualized as being connected continuously to their U=0 position (upper panel). The outstanding difference is that the occupied d_{z^2}+$d_{x^2-y^2}$ weight above the gap converts to predominantly d_{z^2}. This changes corresponds to Co introducing an occupied d_{z^2} majority gap state into the gap at low doping.

FIG. 9: DOS in local coordinates for each Fe in the unit cell of $\mathrm{FeGa_3}$ (top) Mn in $\mathrm{Fe_{0.75}Mn_{0.25}Ga_3}$ (middle) and Fe4 in $\mathrm{FeGa_{2.75}Zn_{0.25}}$ (bottom panel) within mBJ. Half metallicity is broken in the doped cases with the opening of a gap (in contrast to the LDA solutions) change scale!.

The Co ion remains low-spin ($0.14\mu_B$) upon introducing U, whereas the magnetic moment on Fe strengthens from ~ 0.3 to $\sim 1.0\mu_B$. For $U \geq 4$ eV the same effect of shifting of the d-bands is observed when doping with Co, with the Fe moment increasing up to 2.05 μ_B for U= 5 eV. Co remains in its low spin state, with induced moment of $0.2\mu_B$ irrespective of the U value over the range we studied.

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VIII. APPENDIX

Gap closings are of particular interest in these studies of doping. To better represent gap behavior, we have applied the TB-mBJ (mBJ for simplicity) potential functional. For stoichiometric $\mathrm{FeGa_3}$ the band gap value obtained using mBJ is slightly increased with respect to that obtained within LDA (by 0.12 eV, see Table I) with the same features as can be observed in Fig. 9

When electron doped, the experimental and LDA-derived states are half-metallic and that type of solution remains within mBJ. From Table I, for Ge-doped $FeGa_3$, mBJ favors situations where the magnetic moments are disproportionated, being higher in the Fe pair (Fe1/Fe2) closer to the substituted Ge, unlike the LDA solution where the moments were equally distributed among all Fe atoms in the cell). The total magnetic moment in the cell however increases only a little, from 0.9 μ_B to 1.0 μ_B.

For Co-doped $FeGa_3$ within mBJ, there is a slight increase in the magnetic moment of the Fe paired with the Co whose magnetic moment remains unchanged, as do the magnetic moments of the Fe atoms in the other dimer. The total magnetic moment is similarly increased from 0.9 to 1.0 μ_B.

When hole doped, the electronic structure obtained within mBJ is quite different from that derived within LDA. For $Fe_{0.75}Mn_{0.25}$, the state resulting from mBJ consists of a FM ordering within both the Mn-Fe and Fe-Fe pairs whose moments have, however opposite sign as to keep the total magnetic moment in the cell unchanged. The individual moments of Fe/Mn are increased with respect to their LDA values. The resulting state is insulating vs. the half metallic one derived using LDA, the corresponding DOS plot is shown in Fig.9. Clearly, mBJ shifts bands breaking the half metallicity. The gap opening is possible due to the shift of the d_{yz}-like orbital for the minority spin channel above the Fermi level for Mn and its paired Fe. Unlike the LDA result, the mBJ outcomes are consistent with experiments favoring an AFM semiconducting state.

The response obtained for Zn-doped $FeGa_3$ within mBJ is also different to that of LDA. Again, the half metallicity is broken by mBJ and a semiconducting solution takes place for both $x = 0.25$ and 0.5 with the concomitant increase in the magnetic moments as can be seen in Table. I. For $x = 0.25$, the moments of the Fe closer to the substituted Zn increase from 0.40 to 1.0 μ_B. In the other Fe-Fe pair, magnetic moments on the Fe of 0.4 μ_B and opposite sign are induced (non magnetic within LDA). For $x =$ 0.5, in addition to the gap opening, the magnetic ground state consists of a FM ordering in one of the Fe-Fe pairs but AFM in the other. For both doping levels the gap opening is again possible due to the splitting of d_{yz}-like orbital for the minority spin channel of Fe atoms, being shifted above the Fermi level.

As commonly found in other applications, mBJ tends to increase the values of the magnetic moments (Table I).[?] The shifts in the band structure and the concomitant increase in the magnetic moments with respect to LDA are consistent with changes in the charge inside the atomic spheres: increased for Fe and accordingly reduced for Ga atoms.